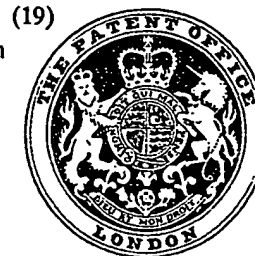


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## (54) METHOD FOR THE PREPARATION OF A GAS MIXTURE HAVING A DESIRED H<sub>2</sub>S/CO<sub>2</sub> RATIO

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention relates to a method for increasing the H<sub>2</sub>S/CO<sub>2</sub> ratio in a gas mixture (hereinafter referred to as the starting gas) in order to prepare a gas mixture having an H<sub>2</sub>S/CO<sub>2</sub> ratio suitable for use in a Claus process (hereinafter referred to as the desired gas).

In many cases it is necessary to remove H<sub>2</sub>S from gas mixtures, for example in order to render these gas mixtures suitable for catalytic conversions using sulphur-sensitive catalysts, or in order to reduce environmental pollution if before or after combustion the said gas mixtures are discharged to the atmosphere.

Examples of gas mixtures from which H<sub>2</sub>S generally has to be removed are gases obtained by complete or partial combustion or gasification of oil and coal, refinery gases, town gas, natural gas, coke-oven gas, water gas, propane and propylene.

In many cases the H<sub>2</sub>S will be removed from the said gas mixtures using liquid absorbents, which will often have a basic character. In a large number of cases the gas mixtures to be purified will also contain CO<sub>2</sub>, at least some of which will be absorbed in the liquid absorbent together with the H<sub>2</sub>S. The H<sub>2</sub>S and CO<sub>2</sub> will be removed from the said gas mixtures at the pressure of the gas mixture concerned, i.e., in many cases at elevated pressure. By heating the loaded liquid absorbent, for example with steam, a gas mixture is obtained consisting substantially of H<sub>2</sub>S and CO<sub>2</sub> in the ratio in which

these substances were present in the loaded liquid absorbent.

This H<sub>2</sub>S and CO<sub>2</sub>-containing gas mixture cannot be discharged to the atmosphere before at least most of the H<sub>2</sub>S has been removed therefrom. The H<sub>2</sub>S is very suitably removed from this gas by converting it into elemental sulphur, which is separated off.

The conversion of H<sub>2</sub>S into elemental sulphur is generally carried out in the art by means of a Claus process in which some of the H<sub>2</sub>S is oxidized to SO<sub>2</sub>, and sulphur and water are formed by reaction of H<sub>2</sub>S with SO<sub>2</sub>, with or without the assistance of a suitable catalyst.

For the operation of a Claus process with a gas mixture comprising substantially H<sub>2</sub>S and CO<sub>2</sub>, the method to be followed depends on the ratio of H<sub>2</sub>S and CO<sub>2</sub> in this gas mixture, or in other words, on the molar percentage of H<sub>2</sub>S based on the total amount of H<sub>2</sub>S and CO<sub>2</sub> present. Three different H<sub>2</sub>S concentration ranges can be distinguished for the operation of a Claus process:

1) If more than approximately 40 mol. % of the gas mixture consists of H<sub>2</sub>S (and the rest is virtually entirely CO<sub>2</sub>), the first stage of the Claus reaction can be carried out by combusting the gas mixture with a quantity of air which is sufficient to convert one-third part of the H<sub>2</sub>S into SO<sub>2</sub>. In one or more subsequent reactors, sulphur and water are then formed, preferably in the presence of a suitable catalyst.

2) If the gas mixture comprising substantially H<sub>2</sub>S and CO<sub>2</sub>, consists of between 15-20 mol. % of H<sub>2</sub>S on the one hand and approximately of 40 mol.% of H<sub>2</sub>S on the other, the above-mentioned method encounters difficulties and the Claus process has to be carried out by separating one-third part of the gas and combusting the H<sub>2</sub>S therein to SO<sub>2</sub>, and subsequently mixing the

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resultant  $\text{SO}_2$ -containing gas with the rest of the  $\text{H}_2\text{S}$ -containing gas, after which the Claus reaction can be further carried out at elevated temperature and preferably in the presence of a catalyst.

3) If less than 15–20% by volume of the gas mixture consists of  $\text{H}_2\text{S}$  (and the rest virtually entirely of  $\text{CO}_2$ ), a Claus process cannot be carried out in the above-mentioned manner. The combustion in the gas mixture has to be additionally supported. This may be effected, for example, by recycling the sulphur formed in the Claus process to the  $\text{H}_2\text{S}$  and  $\text{CO}_2$ -containing gas, or by oxidation of the latter gas with pure oxygen instead of air, or by injecting a fuel (for example a hydrocarbon) into the gas before it is combusted in the thermal stage of the Claus process. These processes are generally expensive and not very attractive technically.

Another possibility to raise the  $\text{H}_2\text{S}/\text{CO}_2$  ratio in the mixture consists in selectively absorbing  $\text{H}_2\text{S}$  from the gas mixture in an appropriate absorbent, and subsequently liberating the  $\text{H}_2\text{S}$  (mixed with the absorbed  $\text{CO}_2$ ) from the loaded absorbent in a regeneration stage. In case the  $\text{H}_2\text{S}$  concentration in the gas mixture is low, an excessive amount of  $\text{CO}_2$  is still absorbed in the absorbent during the selective absorption, when using this method. For that reason it sometimes happens that no gas mixture having the desired composition is obtained after liberation of the absorbed gas from the absorbent loaded in this way.

There is therefore a need for a process whereby the quantity of  $\text{H}_2\text{S}$  is a gas mixture, in particular in a gas mixture otherwise consisting substantially of  $\text{CO}_2$ , can be increased according to desire. It will be endeavoured to control the  $\text{H}_2\text{S}$  content in such a way that either a Claus process can be carried out according to the system described first (addition of air to the entire mixture) or according to the system described second (separation of one-third part of the gas mixture and complete combustion of the  $\text{H}_2\text{S}$  present therein, followed by combination with the rest of the gas mixture).

Because there are in general no great differences between the costs of investment and operation of the embodiments of the Claus process mentioned in 1) and 2), a process whereby the quantity of  $\text{H}_2\text{S}$  is a gas mixture can be increased according to desire will be of importance mainly to increase  $\text{H}_2\text{S}$  concentrations of below 15–20% to 20% or more. At the same time it will be endeavoured not to increase the  $\text{H}_2\text{S}$  concentration much higher than is needed in order to be able to carry out the method of the Claus process described in 2), because higher concentrations do not offer any important advantages in the Claus process,

whereas they do require more absorption and regeneration capacity and energy.

The invention provides a method for the preparation of a gas mixture having a desired  $\text{H}_2\text{S}/\text{CO}_2$  ratio, independent of the originally present  $\text{H}_2\text{S}/\text{CO}_2$  ratio in the starting gas, as a result of which an optimum use of Claus plants and absorbent/regeneration equipment can be obtained.

According to the invention there is provided a method for increasing the  $\text{H}_2\text{S}/\text{CO}_2$  ratio in a gas mixture (hereinafter referred to as the starting gas) in order to prepare a gas mixture having an  $\text{H}_2/\text{CO}_2$  ratio suitable for use in a Claus process (hereinafter referred to as the desired gas), which process is characterized in that  $\text{H}_2\text{S}$  and  $\text{CO}_2$  of the starting gas are absorbed in an aqueous solution of an amine (further to be called an amine liquid absorbent) in an absorption column, in that the absorbed gas is liberated from the resultant loaded amine liquid absorbent in a regeneration column, in that a portion of the gas becoming available from the regeneration column is treated with amine liquid absorbent in an absorption column under such conditions that  $\text{H}_2\text{S}$  is absorbed selectively relative to  $\text{CO}_2$  in the amine liquid absorbent and the loaded amine liquid absorbent obtained in this manner is introduced into the said regeneration column, and in that the magnitude of the said portion of the gas becoming available from the regeneration column is so selected that this gas is the desired gas, and the remainder of the gas becoming available from the regeneration column (further referred to as the resultant gas) is removed.

The method according to the invention may be carried out in a number of different ways, depending on the composition of the starting gas, and on the  $\text{H}_2\text{S}/\text{CO}_2$  ratio in the desired gas.

In addition to  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , the starting gas will generally contain other components, and in a first absorption step the starting gas will be treated with an amine liquid absorbent in which  $\text{H}_2\text{S}$  and  $\text{CO}_2$  are absorbed, while the other gases of the starting gas are not or only slightly absorbed. Such a treatment yields an amine liquid absorbent loaded with  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , the ratio of these gases in the amine liquid absorbent remaining the same or substantially the same as that in the starting gas.

In a number of cases it will be possible to prepare the desired gas according to the invention by introducing the above-mentioned  $\text{H}_2\text{S}$  and  $\text{CO}_2$ -loaded amine liquid absorbent into a regeneration column and to treat a proportion of the gas liberated from the regeneration column, which gas comprises substantially  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , in an absorption column under such conditions that  $\text{H}_2\text{S}$  is absorbed in the amine liquid

absorbent selectively relative to  $\text{CO}_2$ . Such an absorption column is hereinafter also referred to as the selective absorption column. The  $\text{H}_2\text{S}$ -loaded amine liquid absorbent becoming available from the selective absorption column is subsequently supplied to the regeneration column simultaneously with the aforementioned loaded amine liquid absorbent (which will generally be loaded almost exclusively with  $\text{H}_2\text{S}$  and  $\text{CO}_2$ ). Both streams can be introduced into the regeneration column separately, but it is preferred to mix the streams before supplying them to the regeneration column. In the regeneration column the  $\text{CO}_2$  and  $\text{H}_2\text{S}$  are completely or substantially completely removed from the amine liquid absorbent by heating, very suitably by heating with steam.

The gas mixture liberated from the regeneration column must have the desired composition, and this composition will be dependent on the quantity of  $\text{H}_2\text{S}$  which is supplied to the regeneration column in the form of  $\text{H}_2\text{S}$ -loaded amine liquid absorbent originating from the selective absorption column. The latter quantity of  $\text{H}_2\text{S}$  is dependent on the quantity of  $\text{H}_2\text{S}$  supplied to the selective absorption column, because that  $\text{H}_2\text{S}$  is absorbed substantially completely in the amine liquid absorbent in the said absorption column.

Because not more than a portion at most of the  $\text{CO}_2$  is absorbed in the amine liquid absorbent in the selective absorption column, the  $\text{H}_2\text{S}/\text{CO}_2$  ratio in the loaded amine liquid absorbent in the selective absorption column will be far higher than in the aforementioned loaded amine liquid absorbent to be supplied to the regeneration column; as a result the  $\text{H}_2\text{S}/\text{CO}_2$  ratio in the regeneration column and therefore in the gas mixture becoming available therefrom is higher than in the aforementioned loaded amine liquid absorbent to be supplied to the regeneration column. The  $\text{H}_2\text{S}/\text{CO}_2$  ratio in the gas mixture liberated from the regeneration column is consequently determined by the quantity of  $\text{H}_2\text{S}$  supplied from this gas mixture to the selective absorption column; that quantity of  $\text{H}_2\text{S}$  is determined by the portion of the gas mixture liberated from the regeneration column which is supplied to that absorption column.

By controlling the magnitude of the portion of the gas mixture liberated from the regeneration column and supplied to the selective absorption column, it is therefore possible according to the invention to adjust as desired the  $\text{H}_2\text{S}/\text{CO}_2$  ratio in the gas mixture liberated from the regeneration column; this ratio is naturally limited in that the quantity of  $\text{CO}_2$  present in the aforementioned loaded amine liquid absorbent (generally loaded exclusively with  $\text{H}_2\text{S}$  and  $\text{CO}_2$ ) to be supplied to the regeneration col-

umn will invariably be present in the gas liberated from the regeneration column.

In a number of cases it will not be possible to obtain any gas having a desired composition by means of this method, because the ratio of the quantities of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in the starting gas is too low. Also, in certain cases it is possible to obtain a gas having the desired composition, but to that end so large a proportion of the desired gas becoming available from the regeneration column has to be passed to the selective absorption column that the method becomes technically and economically unattractive.

In such cases it is possible to carry out the method according to the invention in another manner. It is then very suitable for the  $\text{H}_2\text{S}$  and  $\text{CO}_2$  absorbed in the amine liquid absorbent from gases containing other components as well, to be liberated from the loaded amine liquid absorbent in a regeneration column. Subsequently, the  $\text{H}_2\text{S}$  in the gas set free from the latter regeneration column (which gas in this embodiment is considered as starting gas), is selectively absorbed in amine liquid absorbent in an absorption column, and the resultant  $\text{H}_2\text{S}$ -loaded amine liquid absorbent is supplied to a regeneration column.

A portion of the desired gas becoming available from the said regeneration column is treated with amine liquid absorbent in a selective absorption column, and the  $\text{H}_2\text{S}$ -loaded amine liquid absorbent obtained from the said selective absorption column is also supplied to the regeneration column.

It is possible to use two absorption columns in which  $\text{H}_2\text{S}$  is selectively absorbed, namely one for the treatment of the starting gas and one for a portion of the desired gas. If desired, the loaded amine liquid absorbent obtained by selective absorption of the starting gas may be introduced into the selective absorption column for the desired gas, where it can serve as absorbent for the said desired gas. In the selective absorption column for the desired gas completely regenerated amine liquid absorbent may optionally be introduced in addition.

It will be clear from the above that by the term "amine liquid absorbent" is meant not only an aqueous solution of an amine containing substantially no gas (i.e., completely regenerated), but also such a solution partly loaded with gas, provided that this load is such that  $\text{H}_2\text{S}$  can still be absorbed from the gas to be treated.

It is generally preferred to use a single selective absorption column in which both the above-mentioned gases, i.e., starting gas and desired gas, are treated with amine liquid absorbent. These gas streams may be introduced into the selective absorption column either together or separately. In the latter case it is advantageous to introduce

the desired gas at a point below the point of introduction of the starting gas.

It may occur that fluctuations in the H<sub>2</sub>S/CO<sub>2</sub> ratio occur with time in the starting gas containing H<sub>2</sub>S and CO<sub>2</sub> in a ratio lower than that desired. In order to keep the H<sub>2</sub>S/CO<sub>2</sub> ratio constant or substantially constant in the gas mixture to be obtained according to the method of the invention, the quantity of gas mixture to be supplied to the selective absorption column will have to be varied (and if desired also the quantity of amine liquid absorbent to be supplied to the said column). It may even occur that the H<sub>2</sub>S/CO<sub>2</sub> ratio in the starting gas is the same or higher than the desired ratio, so that no further H<sub>2</sub>S enrichment of the gas mixture obtained from the regeneration column is necessary. In that case a method according to the invention is not necessary and the introduction of the desired gas into the selective absorption column can be terminated; if the desired gas is the only gas being supplied to the selective absorption column, the said column can be shut down completely.

As an illustration of a process in which the quantity of the gas becoming available and the H<sub>2</sub>S/CO<sub>2</sub> ratio therein may fluctuate, mention may be made of the gasification of coal. First, most of the H<sub>2</sub>S and CO<sub>2</sub> will be removed by non-selective absorption from a gas obtained in this process, and subsequently H<sub>2</sub>S and CO<sub>2</sub> will be liberated from the thus loaded amine liquid absorbent. H<sub>2</sub>S is removed by selective absorption in a selective absorption column from the resultant gas mixture consisting substantially of H<sub>2</sub>S and CO<sub>2</sub>, and by regeneration of the resultant H<sub>2</sub>S-loaded liquid amine absorbent a gas is obtained which under normal process conditions is suitable for a Claus process. If in the case of reduction of the supply of gas obtained by coal gasification and/or decrease of the H<sub>2</sub>S content thereof no gas is obtained which is suitable for the Claus process, it is possible according to the method of the invention to introduce into the said selective absorption column a portion of the gas becoming available from the regeneration column.

The amine liquid absorbent used may be an aqueous solution of primary, secondary and tertiary amines or mixtures thereof. As an example mention may be made of ethanol amine; preference is given to polyalkanol amines, in particular di-isopropanol amine and methyl diethanol amine.

If desired, the aqueous solution of an amine may also contain non-basic compounds capable of physically absorbing H<sub>2</sub>S and CO<sub>2</sub>. Examples of this type of compounds are N-methyl pyrrolidone, methanol and cyclotetramethylene sulphones, in particular sulfolane.

The structure of and the conditions in the

absorption column are so controlled that H<sub>2</sub>S is selectively absorbed from the gas mixture, which otherwise consists largely of CO<sub>2</sub>. The process is very suitably operated countercurrently in a tray column, the gas mixture to be absorbed being introduced at the bottom of the column. The absorption column preferably contains fewer than 20 trays, and the gases are passed through the column at a considerable rate, preferably at a rate of at least 1 m/sec., based on what is known as the "active" or "aerated" surface of the contact tray. If desired, a packed bed absorption column may also be used, having a packed height of preferably less than 10m.

Preferably, the gas mixture to be absorbed is contacted in each selective absorption column with the amine liquid absorbent at approximately atmospheric pressure, although higher and lower pressures are by no means excluded. The temperature of the amine liquid absorbent in the selective absorption column may vary within wide limits; temperatures below 55°C, in particular from 15 to 50°C, are very suitable, although higher temperatures are by no means excluded.

The resultant gas mixture containing H<sub>2</sub>S and CO<sub>2</sub> in the desired ratio (i.e., for use in a Claus process containing either 20 mol. % or slightly more of H<sub>2</sub>S or 40 mol% or slightly more of H<sub>2</sub>S, as explained above) is very suitably subjected to a Claus reaction, in which sulphur is formed. The off-gases from the Claus process, which still contain some H<sub>2</sub>S, can be discharged to the atmosphere after combustion, or their content of sulphur compounds can be further reduced to a considerable extent by reduction and selective absorption in a liquid absorbent of the gas obtained after reduction, for example as described in the published Netherlands patent application 7010604.

The gas becoming available from the selective absorption column, which gas comprises substantially CO<sub>2</sub> but will generally still contain a minor quantity of H<sub>2</sub>S, can also be discharged to the atmosphere after combustion. Combustion and/or discharge thereof may of course be effected together with other sulphur-containing gases, such as the abovementioned Claus off-gases. In case two absorption columns are present, the gas becoming available from the selective absorption column may also (if desired partially) be recycled to the first absorption column.

The invention will now be illustrated with reference to Figs. 1 and 2, each of which represents an embodiment of the invention.

In Fig. 1 a CO<sub>2</sub>-containing gas which must be freed of H<sub>2</sub>S is supplied via a line 1 to an absorption column 2. The purified gas is discharged via a line 3. The H<sub>2</sub>S and CO<sub>2</sub>-loaded amine liquid absorbent is discharged

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via a line 4 and passed to a regeneration column 5. The gas becoming available from the regeneration column 5 via line 6 (the desired gas) is divided into two portions. One portion is discharged via a line 7, for example to a Claus plant 8, the discharge gas of which is discharged to the atmosphere via a line 9, an incinerator 10 and a line 11. The second portion of the gas becoming available from the regeneration column 5 is supplied via a line 12 to a selective absorption column 13 according to the invention. The gas liberated from the said absorption column is either supplied via a line 14 and the line 9 to the incinerator 10, or it is recycled via a line 19 to absorption column 2. The H<sub>2</sub>S-loaded amine liquid absorbent obtained from the absorption column 13 is supplied to the line 4 via a line 15. At the point where the line 6 branches into the lines 7 and 12 there is a mechanism by means of which the distribution of the gas stream from the line 6 between the lines 7 and 12 can be controlled.

The amine liquid absorbent becoming available from the regeneration column via a line 16, which absorbent is free or substantially free of CO<sub>2</sub> and H<sub>2</sub>S, is supplied via lines 17 and 18 to the absorption columns 2 and 13, respectively.

In Fig. 2 a gas comprising substantially H<sub>2</sub>S and CO<sub>2</sub> is supplied via a line 101 to a selective absorption column 102. The gas issuing from the said absorption column is discharged via a line 103, and, because it still contains only very little H<sub>2</sub>S, it may, if desired, be discharged to the atmosphere after combustion. The H<sub>2</sub>S and CO<sub>2</sub>-loaded amine liquid absorbent is passed via a line 104 to a regeneration column 105. The gas becoming available from the said column via a line 106 (the desired gas) is divided into two portions. One portion is discharged via a line 107, for example to a Claus plant (now shown). The second portion of the gas becoming available from the regeneration column 105 is supplied via a line 112 to the selective absorption column 102. The amine liquid absorbent becoming available from the regeneration column 105, which absorbent is free or substantially free of H<sub>2</sub>S and CO<sub>2</sub>, is passed via a line 117 to the absorption column 102. At the point where the line 106 branches into the lines 107 and 112 there is a mechanism by means of which the distribution of the gas stream between the lines 107 and 112 can be controlled.

#### EXAMPLE I

The reference numerals refer to Fig. 1.

A gas stream of 80,000 Nm<sup>3</sup>/h, comprising substantially H<sub>2</sub> and CO and having an H<sub>2</sub>S content of 0.3 mol. % and a CO<sub>2</sub> content of 7.0 mol. %, supplied via the line 1 to the absorption column 2, which contains 15 contact trays. Via line 17 a 30% by weight solu-

tion of methyl diethanol amine in water is supplied at a rate of 140 m<sup>3</sup>/h, and the gas mixture is treated therewith at a temperature of 45°C and a pressure of 20 bar abs. The purified gas escaping via the line 3 contains 3.3% by volume of CO<sub>2</sub> and 10 ppm by volume of H<sub>2</sub>S. The resultant H<sub>2</sub>S and CO<sub>2</sub>-loaded absorbent, in which the H<sub>2</sub>S/CO<sub>2</sub> molar ratio is 0.078, is supplied via the line 4 to the regeneration column 5. This regeneration column, which contains 14 trays, is heated with steam to a bottom temperature of 110°C, the bottom pressure being 1.4 bar abs. Via the line 6 a gas stream of 4150 Nm<sup>3</sup>/h leaves the regeneration column, of which gas stream 2950 Nm<sup>3</sup>/h is supplied via the line 12 to the absorption column 13, which contains 9 contact trays. A 30% by weight solution of methyl diethanol amine in water is supplied (45 m<sup>3</sup>/h) to this column via the line 18, and the gas mixture is treated therewith at a temperature of 45°C and a pressure of 1.1 bar abs. The gas velocity is 1.5 m/sec. In the loaded absorbent discharged via the line 15, the H<sub>2</sub>S/CO<sub>2</sub> molar ratio is 3.17, and the said loaded absorbent is mixed with the absorbent present in the line 4, which absorbent contains H<sub>2</sub>S and CO<sub>2</sub> in a ratio lower than the desired ratio. Via the line 14 a gas containing 90 mol. % of CO<sub>2</sub>, 10 mol. % of H<sub>2</sub>O and 1500 ppm by volume of H<sub>2</sub>S is discharged from the absorption column 13.

As a result of the method according to the invention, the H<sub>2</sub>S/CO<sub>2</sub> ration, which was 0.078 in the absorbent in the line 4, has been increased to 0.28 in the gas mixture becoming available from the regeneration column via the line 6. The said gas mixture contains 20 mol. % of H<sub>2</sub>S, 70 mol. % of CO<sub>2</sub> and 10 mol. % of water. It is supplied to a Claus plant 8 via a line 7.

The absorbent freed of CO<sub>2</sub> and H<sub>2</sub>S and becoming available from the regeneration column 5 via the line 16 is supplied to the absorption columns 2 and 13 via the lines 17 and 18, respectively.

#### EXAMPLE II

The reference numerals refer to Fig. 2.

A gas stream of 10,000 Nm<sup>3</sup>/h, comprising 90% by volume of CO<sub>2</sub>, 7% by volume of H<sub>2</sub>O, 2% by volume of hydrocarbons and 1% by volume of H<sub>2</sub>S, is introduced between the eighth and ninth tray from the bottom of the absorption column 102 (which contains 18 trays). The pressure in the column is 1.05 bar abs. and the temperature 40°C. The gas becoming available from this column via the line 103 (9,790 Nm<sup>3</sup>/h) still contains 100 ppm by volume of H<sub>2</sub>S and further 91% by volume of CO<sub>2</sub>, 7% by volume of H<sub>2</sub>O and 2% by volume of hydrocarbons. The loaded absorbent in column 102, comprising a 24% by weight solution of methyl diethanol amine in water, is introduced via the line

104 into the 12-tray regeneration column 105. The regeneration column is heated with steam to a bottom temperature of 110°C, the pressure being 1.4 bar abs. From this column via the line 106 the desired gas becomes available at a rate of 2260 Nm<sup>3</sup>/h and having a composition of 47% by volume of H<sub>2</sub>S, 47% by volume of CO<sub>2</sub> and 6% by volume of H<sub>2</sub>O. Of this gas, 210 Nm<sup>3</sup>/h is discharged via the line 107 to a Claus plant, and 2050 Nm<sup>3</sup>/h is introduced below the first tray from the bottom of absorption column 102 via the line 112. The gas velocity in this column is 1.5 m/sec. The absorbent regenerated in the regeneration column 105 is supplied via the line 117 to the absorption column 102 at a rate of 110 m<sup>3</sup>/h.

#### WHAT WE CLAIM IS:-

1. A method for increasing the H<sub>2</sub>S/CO<sub>2</sub> ratio in a gas mixture (hereinafter referred to as the starting gas), in order to prepare a gas mixture having an H<sub>2</sub>S/CO<sub>2</sub> ratio suitable for use in a Claus process (hereinafter referred to as the desired gas), characterized in that H<sub>2</sub>S and CO<sub>2</sub> of the starting gas are absorbed in an aqueous solution of an amine (further to be called an amine liquid absorbent) in an absorption column, in that the absorbed gas is liberated from the resultant loaded amine liquid absorbent in a regenerated column, in that a portion of the gas becoming available from the regeneration column is treated with amine liquid absorbent in an absorption column under such conditions that H<sub>2</sub>S is absorbed selectively relative to CO<sub>2</sub> in the amine liquid absorbent and the loaded amine liquid absorbent obtained in this manner is introduced into the said regeneration column, and in that the magnitude of the said portion of the gas becoming available from the regeneration column is so selected that this gas is the desired gas, and the remainder of the gas becoming available from the regeneration column (further referred to as the resultant gas) is removed.

2. A method as claimed in claim 1, characterized in that H<sub>2</sub>S from the starting gas is absorbed in the amine liquid absorbent selectively relative to CO<sub>2</sub>.

3. A method as claimed in any one of claims 1-2, characterized in that the starting gas and the desired gas are treated in the same absorption column simultaneously with the amine liquid absorbent.

4. A method as claimed in claim 3, characterized in that the starting gas and the de-

sired gas are introduced into the absorption column at different points.

5. A method as claimed in claim 4, characterized in that the desired gas is introduced into the absorption column at a point below the point of introduction of the starting gas.

6. A method as claimed in any one of the preceding claims, characterized in that the absorption column in which the desired gas is treated with the said amine liquid absorbent contains few than 20 contact trays.

7. A method as claimed in any one of the preceding claims, characterized in that the gas velocity in the absorption column in which the desired gas is treated with the said amine liquid absorbent, is at least 1m/sec.

8. A method as claimed in any one of the preceding claims, characterized in that the temperature of the amine liquid absorbent in the absorption column in which the desired gas is treated with the said amine liquid absorbent is from 15 to 50°C.

9. A method as claimed in any one of the preceding claims, characterized in that the desired gas is treated at approximately atmospheric pressure with the amine liquid absorbent.

10. A method as claimed in any one of the preceding claims, characterized in that the amine liquid absorbent consists of an aqueous solution of a polyalkanol amine.

11. A method as claimed in claim 10, characterized in that the polyalkanol amine is di-isopropanol amine.

12. A method as claimed in claim 10, characterized in that the polyalkanol amine is methyl disthanol amine.

13. A method as claimed in any one of the preceding claims characterized in that the aqueous solution of an amine also contains sulfolane.

14. A method as claimed in any one of the preceding claims, characterized in that the resultant gas mixture having a desired H<sub>2</sub>S/CO<sub>2</sub> ratio is subjected to a Claus process.

15. A method as claimed in claim 1, substantially as described with special reference to the Examples.

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COMPLETE SPECIFICATION

2 SHEETS

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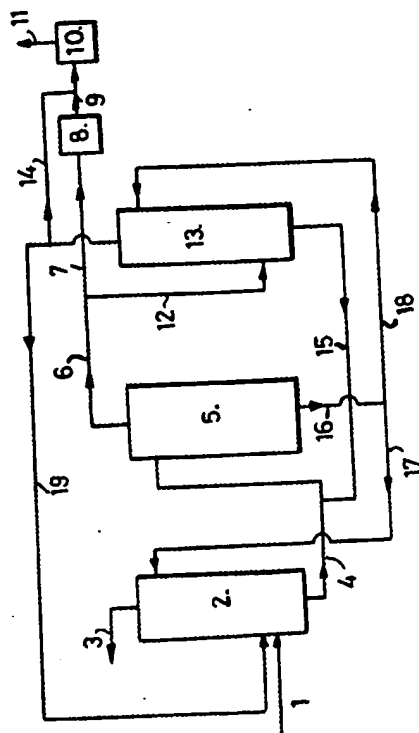


FIG. 1

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COMPLETE SPECIFICATION

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Sheet 2

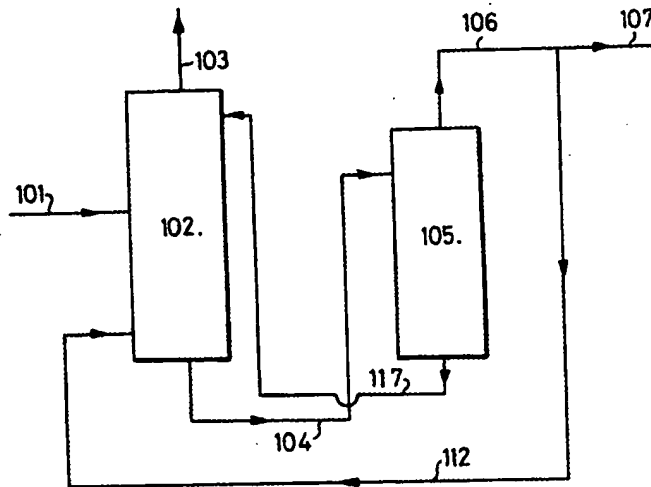


FIG. 2